Electrochemical Oxidation and STM Observations of Squaraine Dye Layers on HOPG Electrodes

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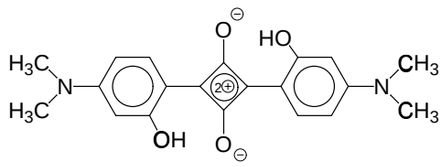
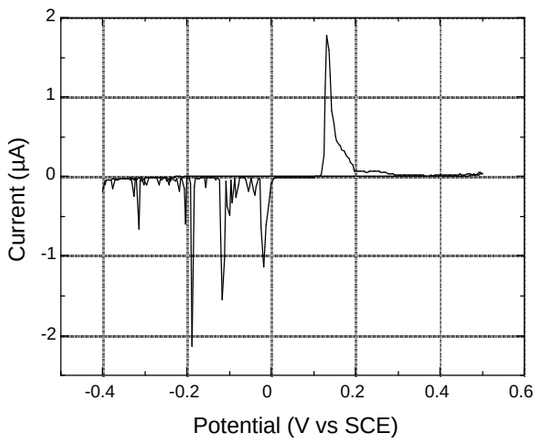
Electrochemical reactions of insoluble highly ordered squaraine (1-1OHSQ) dye layers (see structure below) adsorbed on highly oriented pyrolytic



graphite (HOPG) electrodes were studied in aqueous electrolytes. Staircase cyclic voltammetry obtained in chloride electrolytes revealed hysteresis characterized by large peak separations (100 – 200 mV) and sharp redox peaks (fwhm 10 – 60 mV) the shape and potentials of which depended on electrolyte concentrations. A number of small stochastic reduction peaks were observed at more negative potentials (see figure). We interpret the current spikes to be associated with the reduction of small domains or crystallites of the oxidized 1-1OHSQ layers. Peak potentials and peak shapes were also dependent on the identity of the electrolyte anion species. The results support a reaction scheme where electrolyte anions are incorporated into surface confined one-electron oxidized dye molecular layers. From the results of peak potential shifts, the preference for ion-pairing is estimated to be in the order of: $I^- > Br^- > Cl^- > SO_4^{2-} \approx ClO_4^- \approx F^-$. *Ex-situ* STM observations were performed to reveal structural changes upon electrochemical oxidation of 1-1OHSQ layers in LiCl electrolytes. Two polymorphs with different angles of the long-axis of molecules to the directions of the molecular row were observed for the oxidized samples. Both polymorphs had smaller packing densities compared to the reduced form of the dye.



Cyclic voltammogram of 1-1 OHSQ on an 0.2 cm^2 HOPG electrode in 0.1 M LiCl. The scan rate was 10 mV/s.

The positions of the anions, incorporated into the 2D structure upon oxidation of the layer, are assigned based on the STM images of the layers. Recent results with a hexyl substituted squaraine will also be presented.